

The oxidation of pyrite

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Abstract

The oxidation of pyrite ore in air was studied using a fixed-bed flow reactor. Under isothermal conditions, this oxidation showed a maximum rate during the initial stage and a linear decreasing rate thereafter, and the fractional oxidation versus time curves were in good agreement with a shrinking unreacted-core model. The oxidation rate was affected by the particle size of the pyrite ore. A large particle showed a small initial reaction rate and a large activation energy. Besides, the rate-determining step of a large particle was found to be an interface reaction process while for fine particles it is a diffusion process.

1. Introduction

The oxidation of pyrite ore has been investigated by various workers using a thermoanalytical method, but no concurrent results about the reaction temperature and mechanism were obtained [1]. This is due to the lack of consideration of the effect of the diffusion process on the rate-determining step of the oxidation reaction which involves solid and gaseous reactants. That is, the thermal analyses are usually performed under the condition of stagnant circumstances of reactive gases in a solid sample which is layer-packed in a sample holder. Jorgensen et al. [2] reported the effect of particle size, heating rate and gas diffusion in a crucible on the thermal analysis of pyrite oxidation.

In this paper, two different experimental methods were adopted to eliminate the effects of heat and mass transfer on the oxidation of pyrite. One is that the oxidation of pyrite ore was performed in a flowing atmosphere of air using a fixed-bed flow reactor and the other is that the sample was diluted by alpha alumina as a heat diluent. From the obtained reaction rate versus time curves, rate equation, kinetic parameters, and the effect of particle size on the oxidation were estimated.

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2. Experimental

2.1. Materials

The material studied was pyrite-type iron disulfide obtained from the Yanahara Mine in Okayama prefecture and found to contain no marcasite based on X-ray powder diffraction analysis. Since quantitative analysis gave contents of 43.3 wt% iron and 49.9 wt% sulfur, this specimen was determined to contain 93.0 wt% iron disulfide. The major impurities were 1.9 wt% silica, 1.3 wt% barium, 0.96 wt% copper, 0.73 wt% zinc, 0.52 wt% aluminum, 0.49 wt% calcium and so on.

Three size classes of powder were prepared by pulverizing and screening of the pyrite ore: the first class is the fraction which was 48–100 mesh in screen size (this class is described as 'large particle size' from now on (147–295 μm)), the second was 100–200 mesh in screen size (described as 'moderate particle size' (74–104 μm)) and the third was the fraction which passed through a screen size of 325 mesh (described as 'fine particle size' (< 43 μm)). These powdered samples were diluted with five times their weight of alpha alumina for the oxidation experiments. Preliminary experiments showed that the addition of alpha alumina had no chemical effect on the pyrite oxidation over the entire range of our experimental conditions.

2.2. Apparatus and procedure

The 10 mg neat sample was packed in an open crucible and the thermal analysis in air was carried out at a heating rate of 20 °C/min using a Rigaku 'simultaneous DTA–TG analyzer'.

The oxidation reaction experiments were carried out in a fixed-bed flow reactor using a 1 cm inside diameter Pyrex tube under isothermal and dynamical conditions. For the dynamical operations, the heating rate was 2 °C/min. In the case of the isothermal operations, the required temperature could be obtained within 5 min and the temperature was controlled within ± 1 °C. Considering the accuracy of the analysis and the elimination of the heat of reaction, experiments were carried out using air flow rates of 30–130 ml/min and a sample weight of 100–250 mg. The reaction rate of oxidation was estimated by gas chromatographical analysis of the evolved gaseous sulfur dioxides.

3. Results and discussion

3.1. Oxidation of pyrite on heating

DTA and TG curves of pyrite with three different particle size levels in air are shown in Fig. 1. From these results, the oxidation of pyrite ore was observed to proceed at about 325 °C accompanied by the evolution of sulfur dioxide gas and a large heat of reaction. 31–33 wt% of the total weight loss above 700 °C corresponded

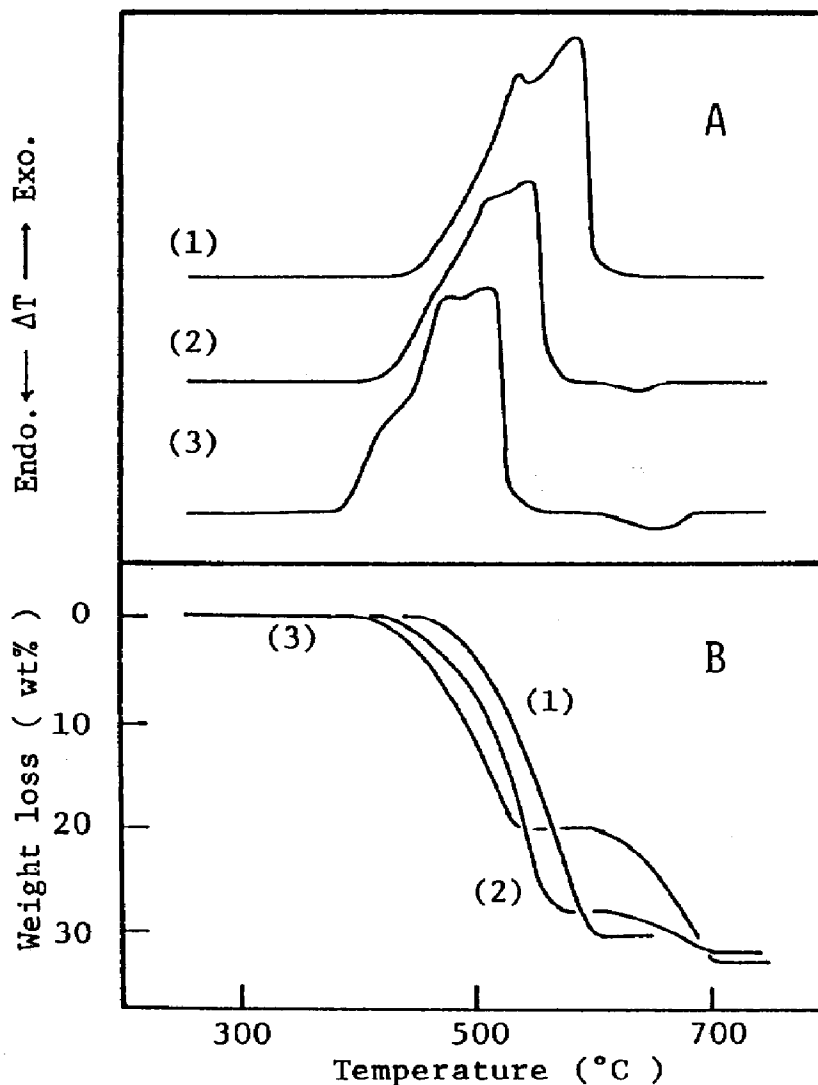


Fig. 1. (A) DTA and (B) TG of pyrite in air. Sample: (1) 147–295 μm , (2) 74–104 μm , (3) < 43 μm .

well to the reaction shown by Eq. (1):



However, the effect of the particle size on the thermal reaction was recognized and the smaller the particle size, the lower the temperature at which the oxidation began. Moreover, reaction products are different with different particle size. In the case of a large particle size (1 in Fig. 1), FeS_2 is entirely oxidized and only $\alpha\text{-Fe}_2\text{O}_3$ was found in the residue immediately after the exothermal reaction. However, the pyrite sample having the smaller particle size (2 and 3 in Fig. 1) was found to show $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , FeS and unoxidized FeS_2 after the reaction which would endothermally decompose at about 640°C. Co-existence of FeS and FeS_2 with $\alpha\text{-Fe}_2\text{O}_3$ was

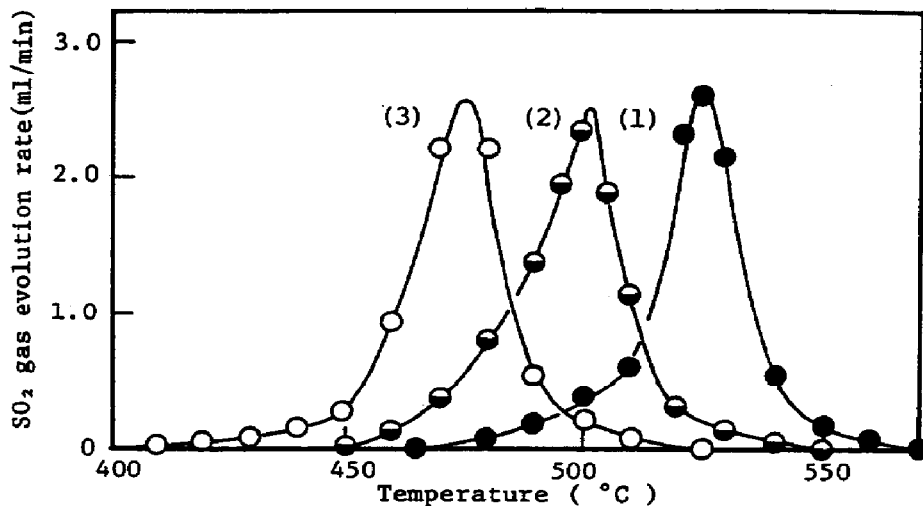


Fig. 2. Oxidation of pyrite in air under dynamical condition (heating rate 2°C/min). Sample: (1) 147–295 μm , (2) 74–104 μm , (3) < 43 μm .

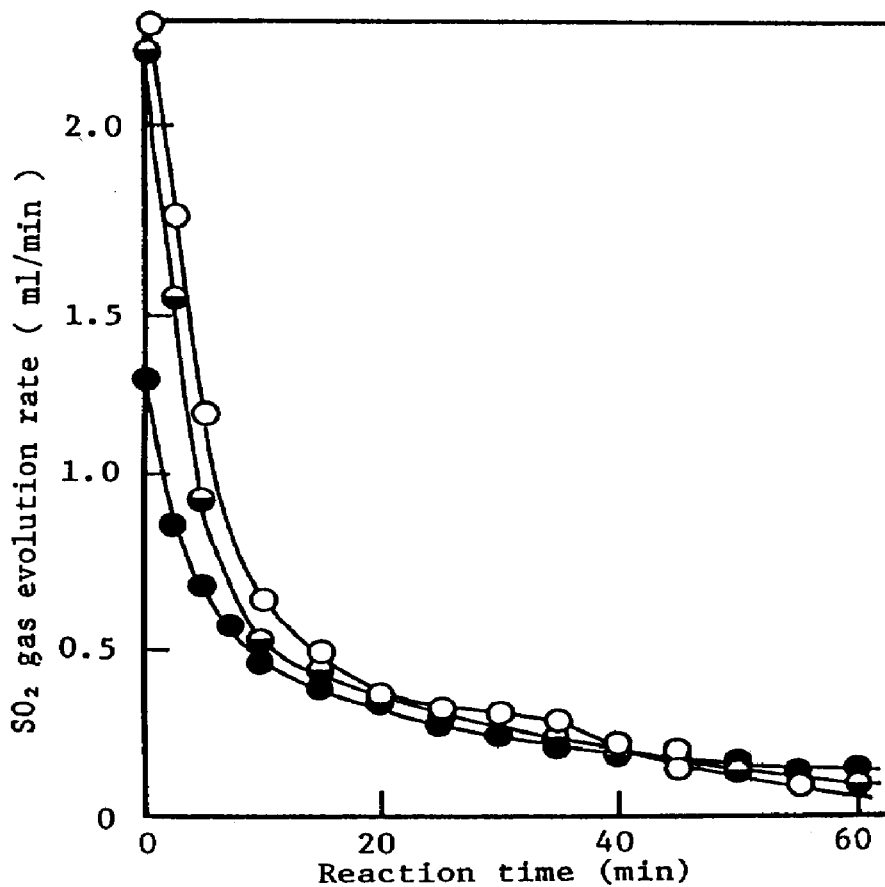


Fig. 3. Isothermal oxidation of pyrite in air. Sample: 74–104 μm ; gas flow rate: 90 ml/min; temperature: (○) 472°C, (◐) 467°C, (●) 460°C.

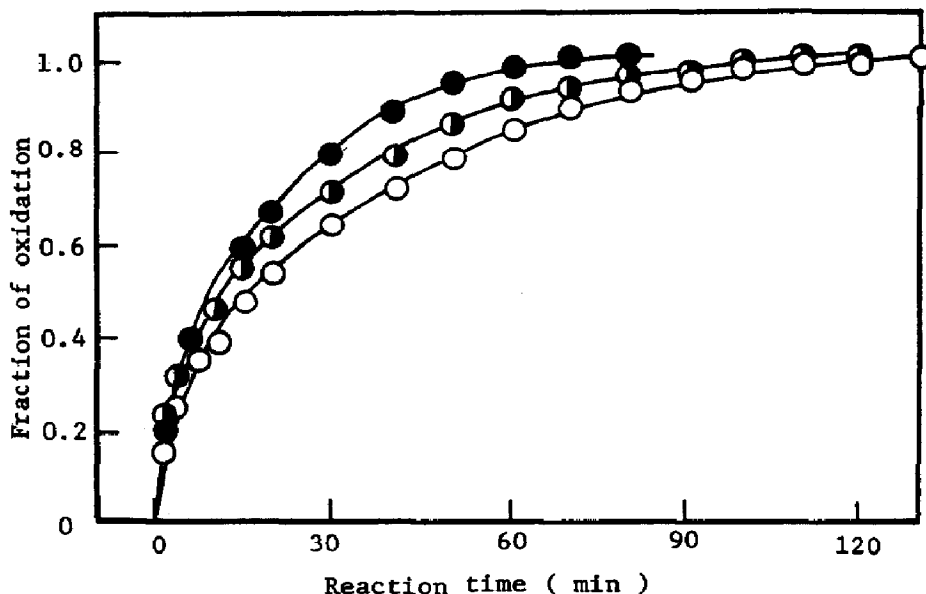


Fig. 4. Isothermal oxidation of pyrite (74–104 μm) in air. Temperature: (●) 472 °C, (◐) 467 °C, (○) 460 °C.

considered because the thermal decomposition of FeS_2 was caused by large heat evolution and imperfect diffusion of oxygen gas. Paulik et al. [3] reported the formation of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2\text{O}_x(\text{SO}_4)_y$ as intermediates in the oxidation of pyrite, but based on X-ray powder diffraction data these intermediates were not detected in the experiment which was conducted in a flow system.

Pyrite oxidation by oxygen in air involves both chemical reaction processes and physical processes such as mass and heat transfers. Thermal analysis has the disadvantage of not being able to eliminate the effect of transport phenomena when studying chemical kinetics. In the present investigation we adopted a gas flow type reactor in order to clarify the chemical kinetics of pyrite oxidation. Fig. 2 shows the sulfur dioxide gas evolution rate versus temperature curves in the case of the oxidation of pyrite during heating at a flow rate of 90 ml/min. As will be described later, this flow rate had no effect on the oxidation rate of pyrite.

Although the temperature at which oxidation commenced similarly depended upon the particle size, the thermal behavior was somewhat different when compared with the result of thermal analysis. That is, the SO_2 gas evolution rate versus temperature curve showed only one peak, signifying that the oxidation proceeded through one step. This was confirmed by the fact that the reaction residue in the course of the oxidation contained only $\alpha\text{-Fe}_2\text{O}_3$ as a product using X-ray powder diffraction analysis and none of the intermediates were detected.

3.2. Isothermal oxidation of pyrite in air

As previously described, heat and mass transfers have some effects on the gas–solid reaction. In this experiment it must be important to eliminate the effects of reactant and product gas diffusion and heat of reaction on the reaction rate. From

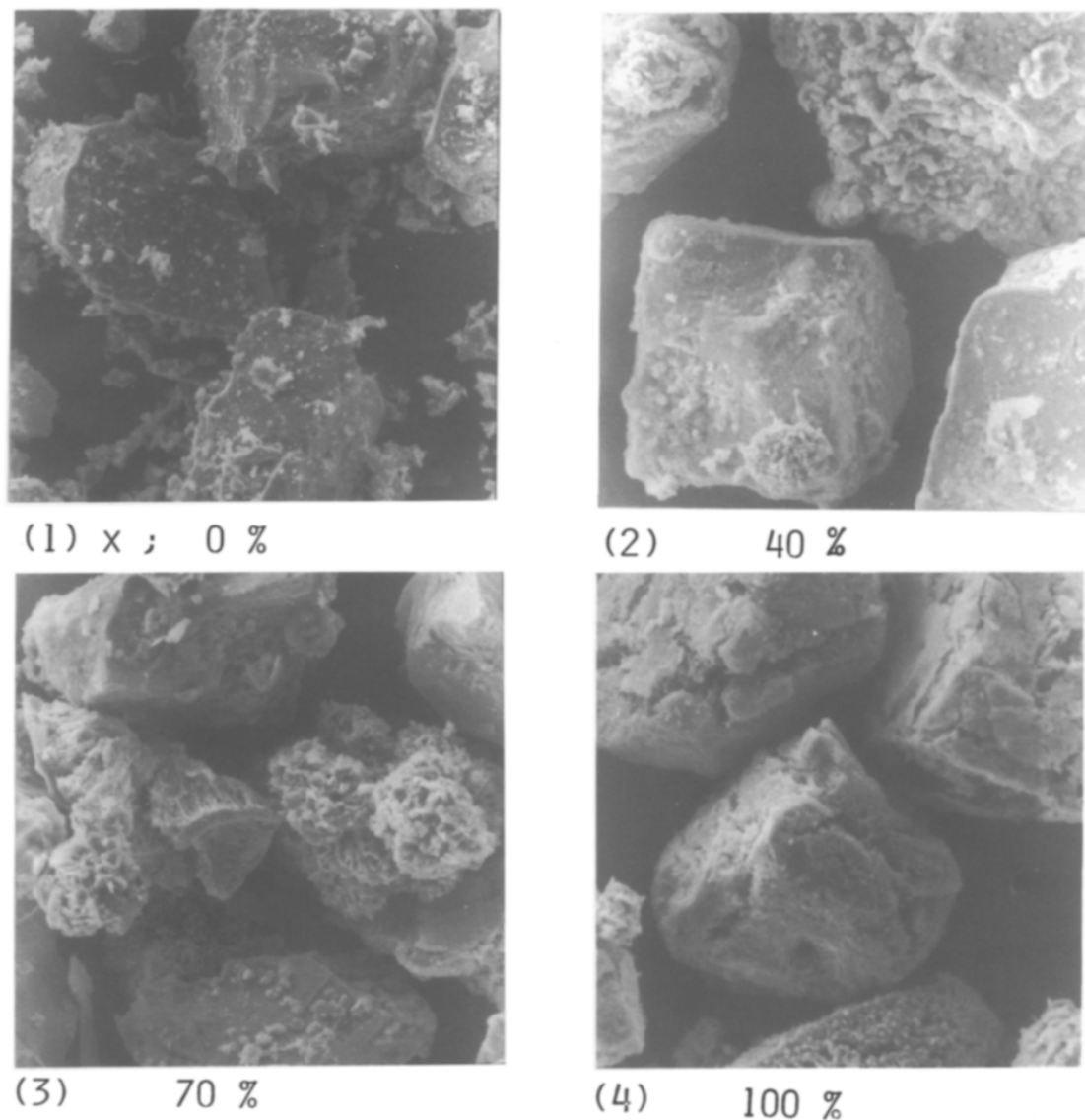


Fig. 5. Observation of pyrite in the course of isothermal oxidation in air (x : fractional oxidation).

preliminary experiments, it was found that at a slow flow rate below 50 ml/min, the reaction rate was influenced by the flow rate, but was independent of flow rate above 70 ml/min. Accordingly, further experiments were carried out at a flow rate of 90 ml/min.

The relation between SO_2 gas evolution rate and the reaction time in the case of pyrite (moderate particle size) oxidation in the temperature range 460–472 °C is shown in Fig. 3. This result indicates that the reaction rate is highest during the initial stage of the oxidation and it decreased linearly thereafter. This linear decrease in the oxidation rate implies that the reaction involves a single step. Graphical integration of Fig. 3 gives the amount of SO_2 gas evolved. The total amount of SO_2 gas evolved

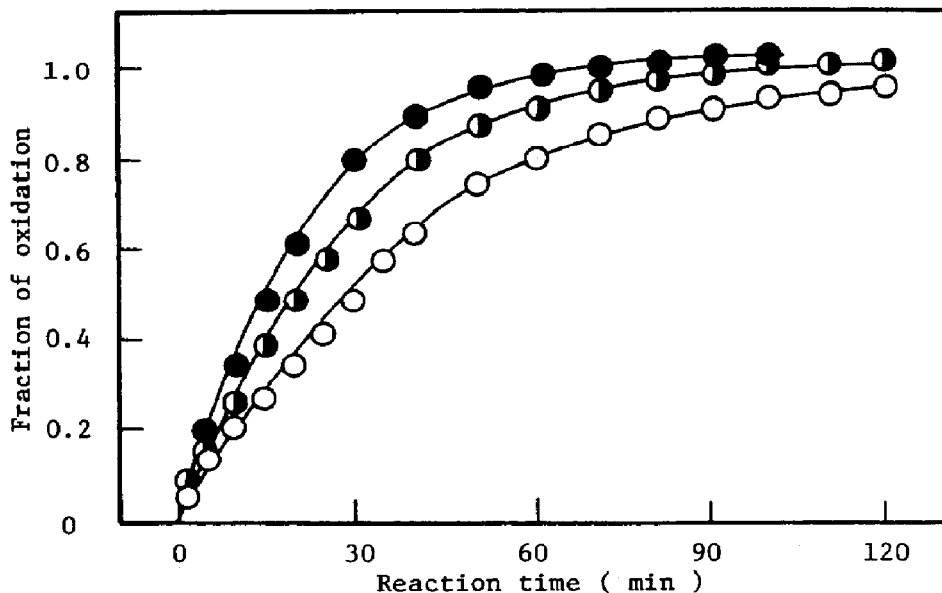


Fig. 6. Isothermal oxidation of pyrite (147–295 μm) in air. Temperature: (●) 500°C, (◐) 495°C, (○) 490°C.

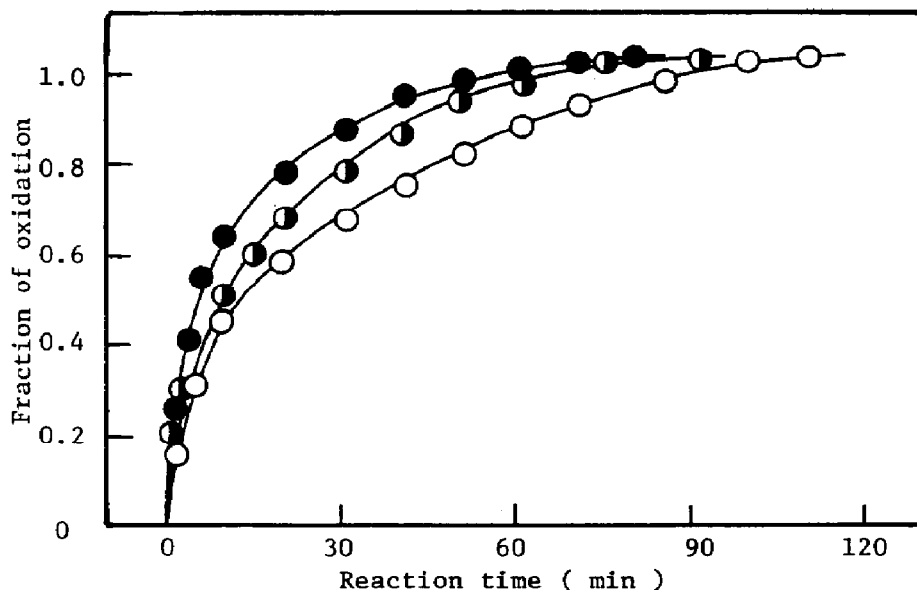


Fig. 7. Isothermal oxidation of pyrite (< 43 μm) in air. Temperature: (●) 445°C, (◐) 430°C, (○) 410°C.

agreed with the SO_2 amount calculated using Eq. (1) within an experimental error of $\pm 5\%$. A fractional oxidation (x) at a time (t) can be determined by dividing the amount of SO_2 from the initiation to time t by the total amount of SO_2 . Fig. 4 shows the fractional oxidation versus time curves of the pyrite (moderate particle size)

Table 1

Rate equations and kinetic parameters for the oxidation of pyrite ore in air

Particle size (μm)	Rate equation $kt =$	Activation energy E_a (kJ/mol)	Preexponential factor (min^{-1})
147–295	$1 - (1 - x)^{1/3}$	370	2.18×10^{25}
74–104	$1 - 3(1 - x)^{2/3} + 2(1 - x)$	199	1.22×10^{12}
< 43	$1 - 3(1 - x)^{2/3} + 2(1 - x)$	97	2.67×10^4

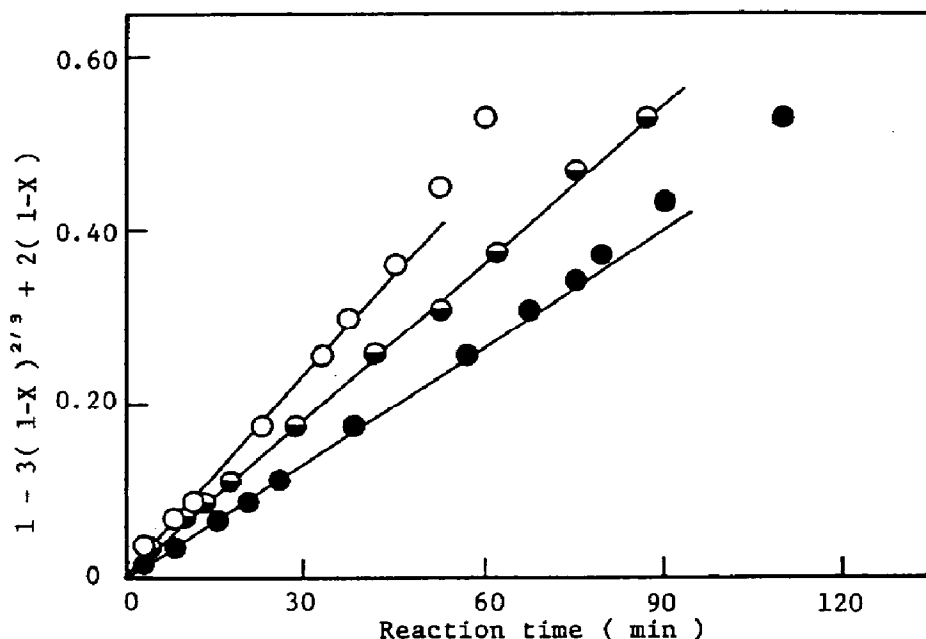


Fig. 8. Plots of a diffusion-controlled shrinking unreacted-core model for pyrite (74–104 μm) oxidation in air. Temperature: (○) 472 °C, (◐) 467 °C, (●) 460 °C.

oxidation. The sample of pyrite ore consisted of particle-like single crystals having several small particles on its surface. Fig. 5 shows some scanning electron micrographs of pyrite (moderate particle size) during the isothermal oxidation at 472 °C. It was observed that although the particle size remained unchanged, micropores and cracks were formed on its surface and in its interior as the oxidation proceeded.

Fig. 6 shows the fractional oxidation versus time curves of the pyrite (large particle size) oxidation in the temperature range 490–500 °C. Similarly as in the oxidation of the moderate particle size sample, the reaction rate was the highest during the initial stage of the oxidation and decreased linearly thereafter. However, compared with the oxidation of moderate particles in Fig. 4, the initial reaction rate was small and the range of temperature which gave a moderate reaction time became

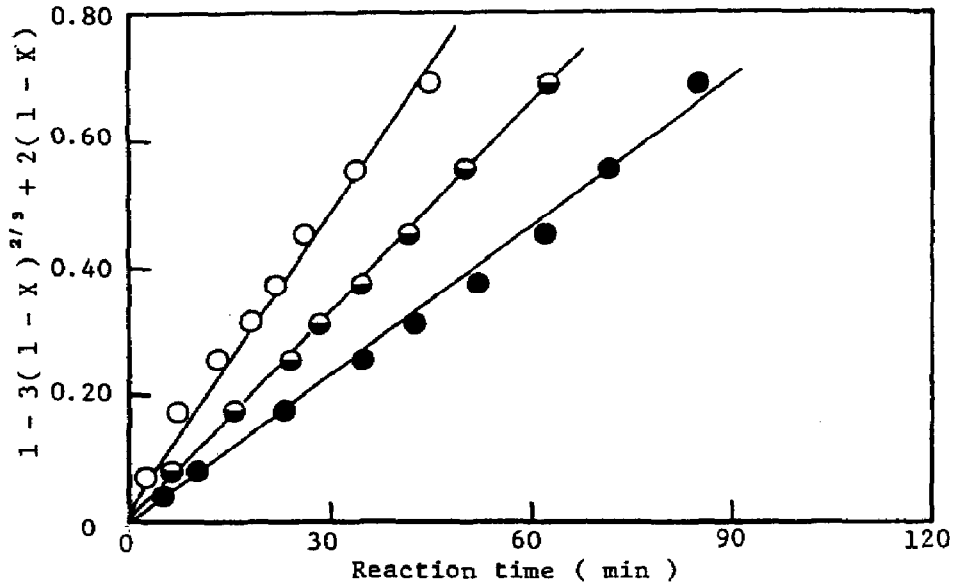


Fig. 9. Plots of a diffusion-controlled shrinking unreacted-core model for pyrite (< 43 μm) oxidation in air. Temperature: (○) 445°C, (◐) 430°C, (●) 410°C.

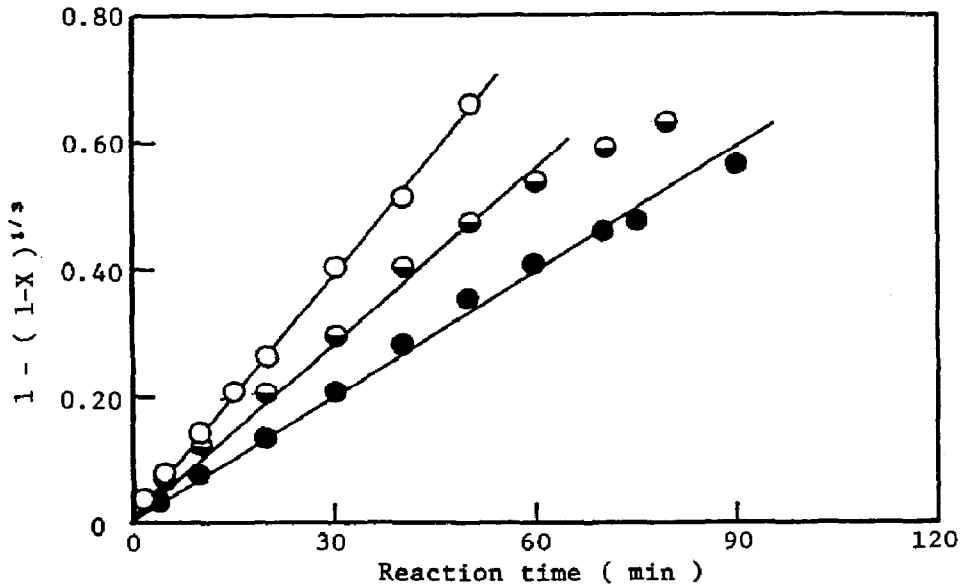


Fig. 10. Plots of a surface reaction-controlled shrinking unreacted-core model for pyrite (147–295 μm) oxidation in air. Temperature: (○) 500°C, (◐) 495°C, (●) 490°C.

somewhat narrow. This can be considered to be due to the reaction involving a high activation energy process. Fig. 7 shows the fractional oxidation versus reaction time curves in the case of pyrite (fine particle size) oxidation in the temperature range 410–445°C. As in the previous two cases, the reaction rate is the highest during the

initial stage of the oxidation, but its initial reaction rate was the largest among the three cases and the range of temperature became wider. This can be considered to be due to the reaction involving a low activation energy process.

3.3. Reaction kinetics of pyrite ore oxidation

As shown in Figs. 4, 6 and 7, the reaction rate was high during the initial stage of the oxidation and decreased linearly thereafter. This reaction is typical for a gas–solid reaction. The entire surface of the pyrite ore is covered with a layer of product in the course of the oxidation and the reaction boundary between products and unreacted layers advances inwards as the oxidation proceeds. In this experiment, the particle size remained unchanged. In view of the results obtained in this experiment, the shrinking unreacted-core model [4] was applied.

The shrinking unreacted-core model for a spherical particle is expressed as the following three equations according to the resistance to the reaction: Eq. (2) when gas-phase mass transfer is the rate-determining step, Eq. (3) when diffusion through the reacted layer is the rate-determining step and Eq. (4) when a chemical reaction at the interface between the reacted and unreacted zone is the rate-determining step,

$$kt = x, \quad (2)$$

$$kt = 1 - 3(1 - x)^{2/3} + 2(1 - x), \quad (3)$$

$$kt = 1 - (1 - x)^{1/3}, \quad (4)$$

where x is the fractional oxidation, t is the reaction time and k is the constant depending upon the temperature and the characteristics of the reaction system (see Table 1).

As shown in Figs. 8 and 9, the present experimental results for the moderate particle size (Fig. 8) and for fine particle size (Fig. 9) samples fit well with Eq. (3), involving a diffusion step as the rate-determining step. On the other hand, Fig. 10 shows the good applicability to the oxidation of the large particle size sample of Eq. (4) involving an interface chemical reaction process as the rate-determining step. These results were explained as follows. Fine particles have many active sites for the oxidation on the surface layer because of an accumulation of mechanical energy from pulverizing. As nucleation for the oxidation easily occurred in such circumstances, a surface chemical reaction process did not produce a reaction resistance and, therefore, a diffusion process determined the reaction rate. In the case of the oxidation of large particles, there are few active sites for a chemical reaction on the surface and, thus, the surface chemical reaction became the rate-determining step.

4. Conclusions

As Jorgensen reported [2], it was determined that heat and mass transfers have an important effect on the oxidation of pyrite in air. Under isothermal conditions, the oxidation showed a maximum rate during the initial stage and a linearly decreasing

rate thereafter. The fractional oxidation versus time curves were in good agreement with a shrinking unreacted-core model. The oxidation rate was affected by the particle size of the pyrite ore. The larger the particle size, the smaller the initial reaction rate and the larger the activation energy became. In addition, the rate-determining step for larger particles was found to be an interface reaction process while for fine particles it is a diffusion process.

5. References

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